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Electrophoretic deposition (EPD) process for lead zirconate titanate (PZT) thick films fabrication and high frequency medical imaging

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Piezoelectric lead-zirconate titanate (PZT) thick films were fabricated on non-flat substrate by electrophoretic deposition (EPD) process for high-frequency ultrasound applications (20 MHz). PZT and PbO particles were stabilized in ethanol and deposited on curved unpoled porous PZT substrate at constant current of 1 mA for 60 seconds. The deposit was sintered at 900°C for 2 hours in a PbO-controlled atmosphere. The thickness of the PZT thick film is 38 µm and the porosity is 20 %. An effective thickness coupling factor of around 37 % and a dielectric constant at constant strain of 660 were measured. A high- frequency single element transducer was fabricated for high resolution medical imaging. It was integrated in an echographic imaging system. High-resolution images of skin *in vivo* were performed which confirm the high potential of using electrophoretic deposition as a method for processing PZT thick film on non-flat substrate for high frequency transducers.

1 Introduction

Ultrasonic transducers are widely used for medical investigations and diagnosis. For imaging biological tissues such as skin, eye, small animals or for intravascular examinations, the transducer generally operates in a frequency range between 20 and 50 MHz [1, 2].

Basically, a single element transducer consists of a piezoelectric element, one or several matching layers, a lens to focus the acoustical beam and a backing. The piezoelectric material is the most important part of the transducer; it converts electrical waves into mechanical ones or vice versa. The piezoelectric properties of the material coupled with its geometry define the properties of the transducer, especially the operating center frequency, the sensitivity and spatial resolution (axial). Lead zirconate titanate (PZT) is commonly used as piezoelectric material due to its high piezoelectric response.

For transducers operating in the high frequency range, the piezoelectric layer is a few tens of micrometers thick and can be deposited by thick film technologies. However, the acoustical beam needs to be focused to increase the lateral resolution. There are two main approaches. First, an acoustical lens can be added to a planar thick film, which implies a significant decrease of transducer sensitivity due to high attenuation through the lens at these frequencies. Second, the piezoelectric film can be patterned on a curved substrate to obtain a geometrical focusing that avoids the use of a lens and consequently the decrease of sensitivity.

In this case, the film cannot be deposited by conventional thick film technologies, such as screen-printing (well adapted for flat substrates). Previous studies were performed to deposit a piezoelectric layer on a curved substrate such as pad-printing [3, 4] or dip-coating [5] processes. In the present work, electrophoretic deposition (EPD) process was developed [6, 7, 8]. It is an adaptive and low cost method that enables the deposition of various materials on conductive substrates by applying a DC electric field [9, 10]. It requires a stable suspension with well dispersed, charged particles. To process homogenous and crack-free thick films with desired thickness and density, the properties of the suspension, the deposition process as well as the sintering procedure need to be optimized [10,11].

The substrate acting as a backing is a golded curved porous PZT ceramics that could be considered as a ceramic-air composite (with closed porosity). Its slightly lower acoustical impedance than that of the thick film will lead to a high bandwidth of the transducer [12].

The motivation of our work was to process piezoelectric PZT thick films with tailored thickness and density on non-flat substrate by electrophoretic deposition. The thickness and density of PZT thick films will be determined and its electromechanical properties will be measured. The transducer will be fabricated and characterized. Skin images obtained with the transducer will be presented.

2 Fabrication process of thick film

The porous PZT substrate used as a backing was fabricated by MEGGITT (Ferroperm Piezoceramics A/S) [3, 12]. The dimensions are described in Figure 1. This substrate based on Pz37 composition was made from a bulk cylinder, which was machined to the specified dimensions. A spherical shaped depression was then machined into one of the faces of the cylinder using a lens grinder. Finally, the gold electrode was painted using a brush.

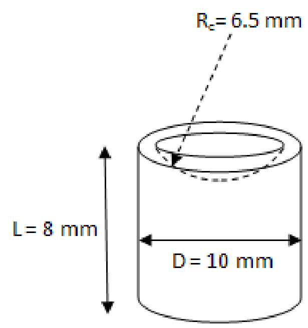

Figure 1: Sketch of the (passive) PZT cylinder used as substrate for the (active) PZT thick film.

2.1 Preparation of PZT suspension

PZT powder with a stoichiometry of $PbZr_{0.53}Ti_{0.47}O_3$ was prepared by solid-state synthesis. PbO (99.9+%, Aldrich), ZrO_2 (99.9%, Tosoh) and TiO_2 (99.9%, Alfa Aesar) were mixed with alcohol in a planetary ball mill for 2 hours. The powder was dried and calcined at 950°C for 2 hours. After the calcination, the powder was milled for 8 hours in an attritor mill.

A PZT suspension with a solid load of 1 vol. % was prepared by homogenizing the PZT powder in anhydrous ethanol (Carlo Erba, Milano, Italy), Polyacrylic acid (PAA) (50 wt. %, Sigma Aldrich), n-butylamine (BA) (99.9%, Alfa Aesar) and ethyl cellulose (EC) (Mv=2000, Sigma Aldrich) were used as additives. The suspensions were homogenized in a $Zr0_2$ planetary mill for 1 hour at 200 rpm.

The deposition was performed from a suspension that was obtained by mixing a PZT suspension with a PbO suspension in a molar ratio corresponding to a stoichiometry of 98 mol % of PZT and 2 mol % of PbO. The PbO suspension was prepared from PbO powder (99.9%, Sigma Aldrich) milled for 4 hours in attritor mill, in anhydrous ethanol and following the procedure of the PZT suspension. In this case the ethyl cellulose was not added.

2.2 Preparation of the piezoelectric thick film

The electrophoretic deposition (EPD) was performed at room temperature in a horizontal electrode cell with a platinum cathode shaped to have the same radius of curvature as the substrate and where the substrate with gold electrode acts as anode. The area of the anode was 50 mm^2. The deposition was performed at 1 mA for 1 min with a distance between the electrodes of 18 mm. Then the film was sintered at 900°C for 2 hours in a lead-rich atmosphere. On the top of this layer, PZT PbO was deposited using identical deposition and sintering conditions.

A gold layer was sputtered for 4 min to obtain a 200 nm thick top electrode. Finally, the thick film was poled at 150°C in oil bath with an electric field of 6 kV/mm for 15 min.

3 Electromechanical characterization

Cross-section of a multilayer structure was made and characterized by scanning electron microscopy (SEM) (JEOL 5800, Tokyo, Japan). From this cross section, the values of the thickness of each layer and the volume fraction of porosity in the PZT substrate and the PZT thick film were deduced. Figures 2 and 3 show the representative microstructure of one of our samples at two different magnifications.

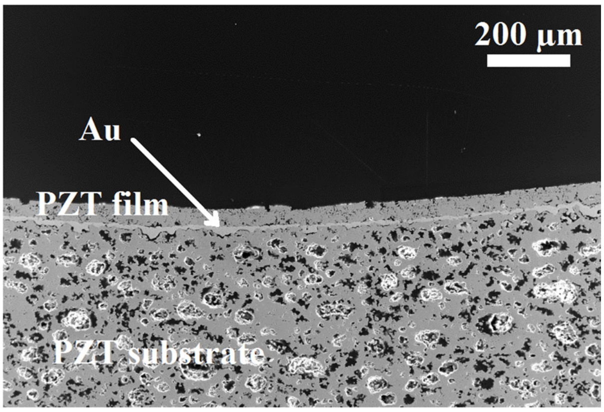

Figure 2: SEM cross section of the microstructure at low magnification to observe the curvature of the structure.

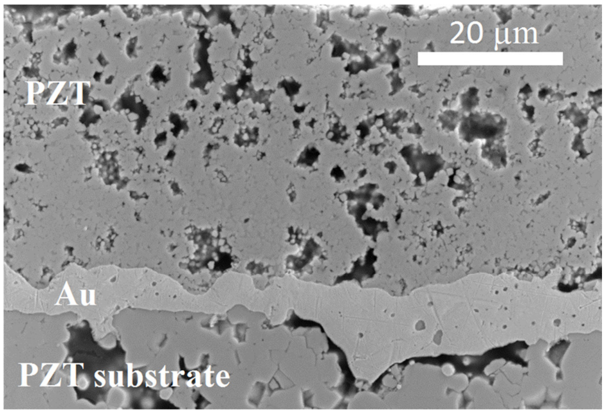

Figure 3 : SEM cross section of the microstructure at high magnification.

These properties of PZT thick-film structure are summarized in Table 1 where the acoustical properties of the constitutive materials are added [13]. The porosity of the substrate has been determined at around 25 % and the porosity of the thick film deposited by electrophoretic deposition at 20 %. These values allow deducing the density, the longitudinal wave velocity and the acoustical impedance from a homogenization model [14].

Table 1: Material properties of layer of the structure.

Layer	Material	t (µm)	C_L (m/s)	ρ (kg/m^3)	Z (MRa)
Front electrode	Gold	0.2	3240	10500	63.8
Thick film	PZT	38	-	6400	-
Bottom electrode	Gold	10	3240	10500	63.8
Substrate	Porous PZT	8000	2700	5800	15.7

t: thickness, C_L: longitudinal wave velocity, ρ: density, and Z: acoustical impedance.

A mean thickness of 10 µm has been measured for the bottom electrode. The electromechanical properties corresponding to the response of the film in thickness mode were deduced by measuring the electrical impedance as a function of frequency. The set-up was composed of an HP4395 vector analyzer and an impedance test kit.

An equivalent electrical circuit model was used (KLM scheme [15, 16]) to simulate the electrical impedance behavior of the thick film structure. Here, the backing (curved porous PZT substrate) of the structure is considered as a semi-infinite medium. The parameters of the four layers from Table 1 are introduced in the KLM model and considered as constants. A fitting process on the experimental complex electrical impedance allows the unknown thickness mode parameters of the piezoelectric thick film to be obtained. The longitudinal wave velocity, the dielectric constant at constant strain, the effective thickness coupling factor and the mechanical losses are obtained. Figure 3 represents the electrical impedance of the structure in air as a function of frequency.

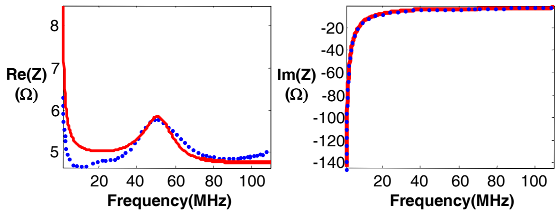

Figure 3: Electrical impedance of the structure in air as a function of frequency around the fundamental resonance (blue points: experimental, red solid line: theoretical).

The effective coupling factor deduced from this procedure is around 37 % and the dielectric constant at constant strain is 660. In this configuration, as observed in Figure 2, the thickness of some of the layers is not uniform (in particular the bottom electrode) which has a significant influence on the resonance behavior of the whole structure. This could lead to an underestimation of the effective coupling factor.

4 Transducers

4.1 Transducer Fabrication

PZT thick-film deposited on non-flat porous PZT backing was used to fabricate a transducer. The two electrical contacts were made with thin copper wires and conductive epoxy resin on each electrode and were connected to a 50 ohms coaxial cable for a first electro-acoustic evaluation (Figure 4).

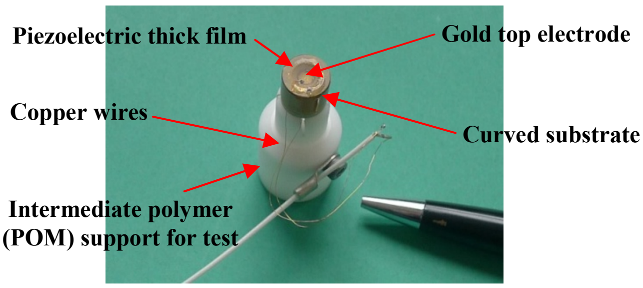

Figure 4: Photograph of the prototype.

Then, the structure was inserted in a polymer housing specially designed to be integrated in a mechanical probe for imaging.

4.2 Transducer characterization

The transducer was characterized in pulse-echo mode on a silicon target in water to avoid preamplifier saturation. The electrical excitation was performed with a home-made broadband generator developed for high resolution medical imaging. A 50 cable with a length of around 20 cm was used. A focal distance of 6.5 ± 0.1 mm was measured; this value corresponds to the radius of curvature of the initial design. Figure 5 represents the pulse-echo response at the focal distance. The value of the *f-number*, *i.e.* the ratio of the focal distance to the transducer diameter, is 2.1.

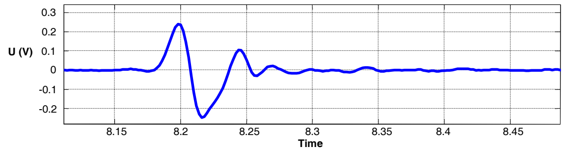

Figure 5: Experimental electroacoustic response in water at the focal distance (6.5 mm).

The corresponding frequency response (Fourier transform of the impulse response), shows the transducer has a center frequency of 20 MHz and a -6 dB relative bandwidth of 110 %

5 Echographic images

The PZT-based transducer prepared by EPD was integrated in a real time ultrasonic scanner (ATYS MEDICAL [17]). The transducer was inserted in the probe (Figure 6) and several *in vivo* images of human forearm skin and nail were recorded with the system (Figure 7).

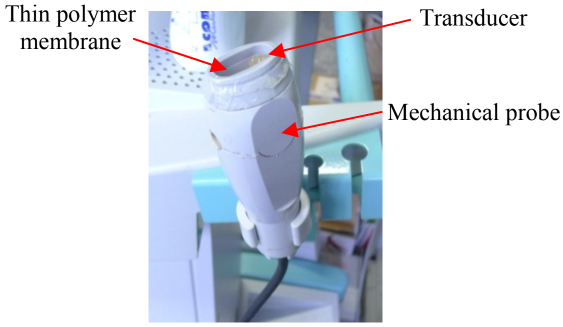

Figure 6: Photograph of the probe with the transducer.

Figure 7: Photograph of the high frequency (20 – 50 MHz) ultrasound imaging system [17] (for *in vivo* human forearm skin images).

In Figure 8 the images are represented: (a) normal skin of a forearm, (b) naevus on a human forearm and (c) base of a fingernail. High axial resolution (due to high bandwidth) and lateral resolution (due to low f-number) allowed good image quality to be obtained despite the relatively low centre frequency. However, due to this low f-number (around 2), the drawback as expected is a relatively short depth of field.

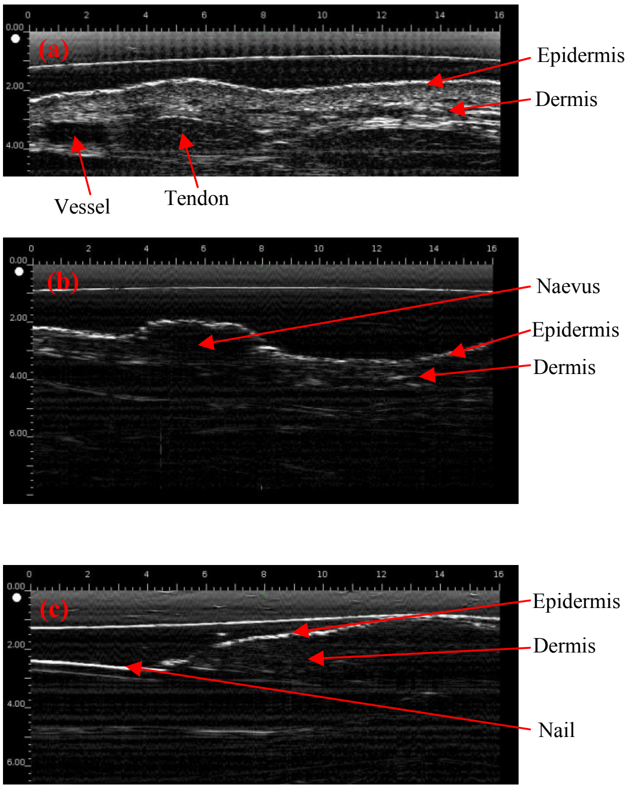

Figure 8: High resolution *in vivo* images of (a) normal human forearm skin, (b) naevus on human forearm skin, (c) base of a fingernail (image dimensions are around 4mm×16 mm).

6 Conclusion

The electrophoretic deposition process has been used for processing of piezoelectric thick films on non-flat substrates. The PZT layer was characterized and sufficiently high electromechanical properties (k_t around 37 %) to produce efficient ultrasonic transducer structures were obtained. The corresponding high frequency transducer has a center frequency at 20 MHz and a -6 dB relative bandwidth at 110% which leads to high spatial resolutions. *In vivo* high-resolution echographic skin images were produced. These results demonstrate that electrophoretic deposition is a suitable fabrication method to prepare high-quality, low-cost high frequency transducers.

Acknowledgments

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